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SO_2 AND NO_2 MEASUREMENTS SOUTHERN CALIFORNIA 18-22 OCTOBER 1971

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Research Triangle, North Carolina

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Independent remote-sensing data were desired for comparisons to final acceptance tests of infrared remote sensors. A dual-gas correlation spectrometer was used to measure sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) simultaneously. On October 18, 19, 20, and 21, 1971, perimeter measurements were made in the general vicinity of an industrial area in Southern California. On October 22 a comparison was made between the COSPEC II Correlation Spectrometer and the COSPEC III version.

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SO_2 AND NO_2 MEASUREMENTS SOUTHERN CALIFORNIA 18-22 OCTOBER 1971

INTRODUCTION

Final acceptance tests of infrared remote sensors produced by the General Dynamics Company were undertaken in the vicinity of an oil refinery in Southern California between 18 and 22 October 1971. Independent remote-sensing data were desired for comparisons at this extended source. This report covers the second phase of work contracted to Environmental Measurements, Inc. for the use of the Barringer Correlation Spectrometer. Earlier work, in the vicinity of a power plant, was undertaken in mid-July 1971.

A dual-gas correlation spectrometer was used to measure sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) simultaneously. On October 18, 19, 20, and 21, 1971 perimeter measurements were made in the general vicinity of an industrial area in Southern California. On October 22 a comparison was made between the Environmental Protection Agency's COSPEC II Correlation Spectrometer and the COSPEC III version operated by Environmental Measurements, Inc. (EMI).

Results of this work are reported as Task A of contract #68-02-0124.

EQUIPMENT AND PROCEDURES

The principal equipment used was the newly introduced Barringer Research COSPEC III™ Dual-Gas Correlation Spectrometer (Figure 1).

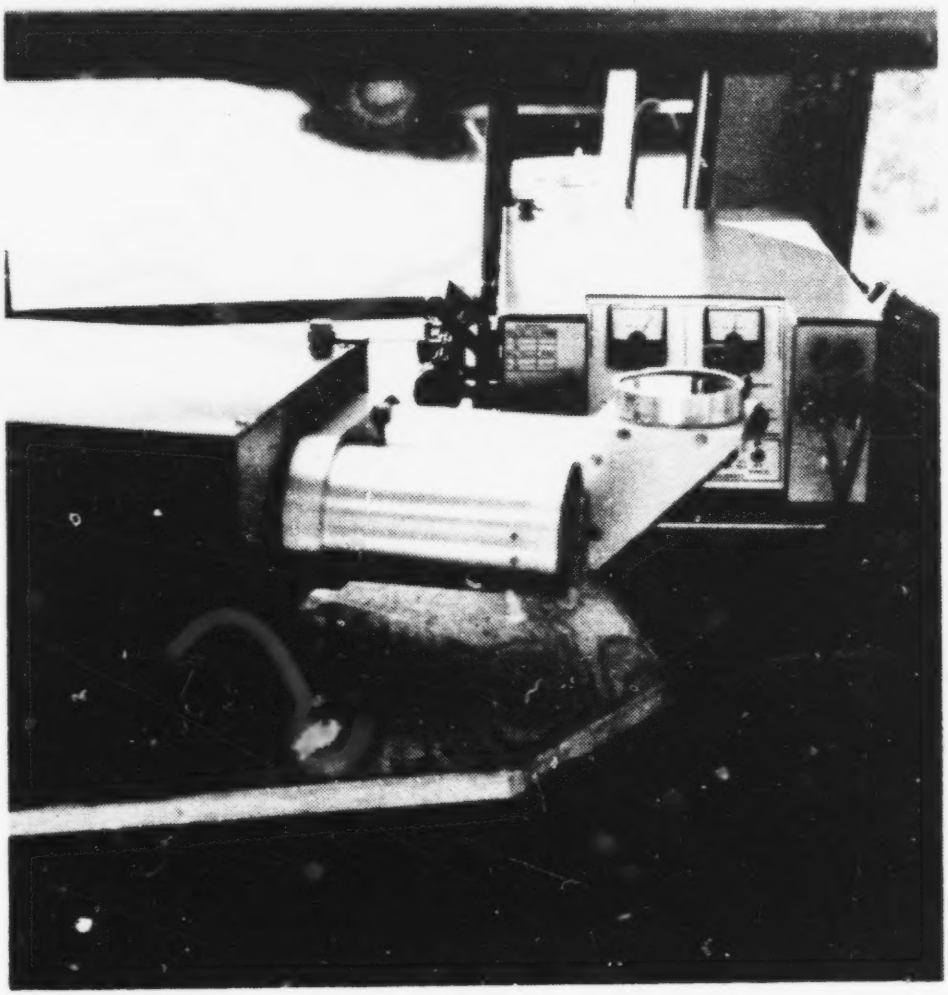

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FIGURE 1

TWO BARRINGER COSPEC™ DUAL GAS CORRELATION SPECTROMETERS MOUNTED FOR VERTICAL-VIEW BURDEN SURVEY

This portable remote-sensing instrument is intended for quantitative measurement of SO_2 and NO_2 in an optical path between a suitable source of visible and ultraviolat radiant energy, such as Rayleigh-scattered daylight illumination or a quartz iodide or xenon lamp. The COSPEC III differs from the COSPEC II principally in that it has an "active" mode of operation; that is, COSPEC III can be set to operate on a modulated light source enabling around-the-clock data.

The Cospec instrument consists of a telescope to collect light from the distant source, a two-grating spectrometer for dispersion of this incoming light, a disc-shaped multiple-slit mask and an electronics system. The disc "correlator" functions as a high contrast reference spectrum for matching against the incoming absorption spectra and is comprised of rays of circular slits photo-etched in aluminum on quartz. These slit arrays are designed to correlate with, sequentially in a positive and negative sense, the absorption bands of the target gas by rotation of the disc in the exit plane. The light modulations so produced are detected by photomultiplier tubes and processed in the electronics to produce a voltage output which is proportional to the optical depth or burden (parts per million-meters) of the gas cloud under observation. The system automatically compensates for changes in varying source light intensity for each channel.

In the passive application, the instrument is principally used in an upward-looking (vertical) mode of operation. In such a configuration the analog records, produced on a two-channel strip chart recorder, represent the total burden of gas overhead:

$$\text{ppm-m} = \frac{\text{gram-meters}}{\text{cubic meters}} = \frac{\text{grams}}{\text{square meter}} \text{ (total burden)}$$

A knowledge of the wind velocity enables computation of the total flow of gas over the route. If the total burden includes the plume of a single stack or an industrial site, this calculation results in total emission rates. It is not necessary to enter the source property. Normally a set of roads is selected which completely encircles the source to be studied. Several perimeter traverses are conducted around the isolated area, and simultaneously wind velocity measurements are made. The mass flow (M) across each of the boundary roads of the source is calculated by:

$$M = LvG$$

where M = mass flow (grams/second)
L = length of straight traverse section (meters)
v = wind velocity (meters/second)
G = average total burden (grams/square meter)

By adding all of the out-of-the area rates and subtracting the into-the-area rates, a net rate of average gas production is determined. By repeating the traverse a number of times a statistical sample is obtained which reduces errors due to

the finite traverse times and the changes in wind condition.

Without question wind is the dominant variable in measuring emissions.

The second principal use of the spectrometer during these tests was in the long-line or long-path mode of operation. A xenon light source was set some 1200-meters distant and focused on the spectrometer. This light source is modulated at approximately 2200 hertz and is viewed by both telescopes on the spectrometer. The narrower Maxwellian cassegrain scope focuses on the beam of light. The second direct-viewing telescope is focused on a photo-diode which senses the modulation rate. This signal is amplified and utilized as the reference for a narrow-band filter, which enables the COSPEC III to observe only the absorption present on the modulated light. Data obtained in this fashion represent the spatially integrated concentration of gas along the line of sight. The concentration-pathlength is divided by the distance between the source of light:

$$\frac{\text{ppm-m}}{\text{m}} = \text{ppm} = \frac{\text{grams}}{\text{m3}}$$

Absolute levels of gas concentration are obtained by measuring the gas levels over a very short path to determine zero levels. Variations of the gas levels are obtained directly on the chart record.

For mobile work, the EMI COSPEC III was mounted in a Volkswagon microbus together with a two-pen Model EPR-3 Weather Measure Strip Chart Recorder and a Cornell-Dubilier Sign-wave Inverter. A power generator was used to supply power to the equipment for long-term long-line measurements.

This system is calibrated by placing quartz cells containing known quantities of the target gas in the line-of-sight within the instrument. These calibrations are made periodically and used to quantify the resulting data.

RESULTS, TASK A

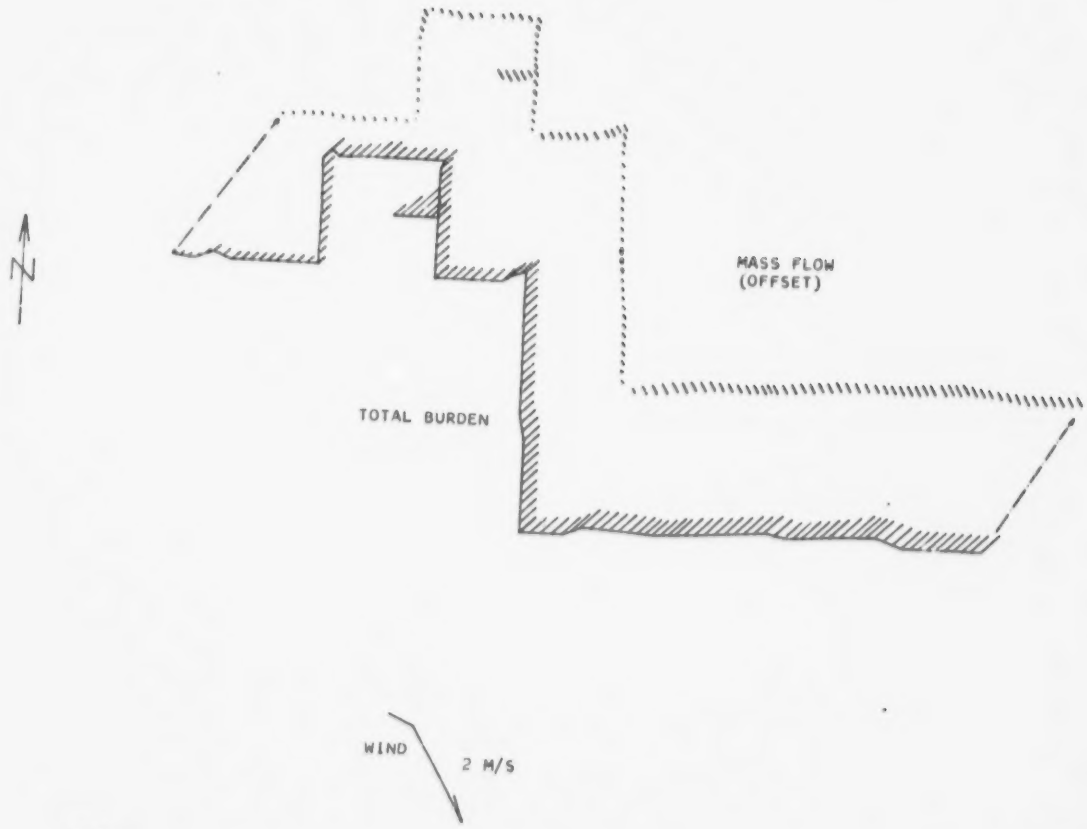
REGIONAL SURVEYS

During the first two days a number of perimeter and regional measurements were conducted in and about an oil-refinery complex in Southern California. These data have been digitized and total burden and mass flow maps were produced by computer for all the data gathered. Wind data used in their display were gathered from the local airport, a site varying from 6 to 15 miles to the northwest of the survey area.

18 OCTOBER 1971

After installation of the correlation spectrometer in the microbus, the equipment was driven along the route shown in Figure 2. The site was partially encircled, and the wind was from the northwest at the beginning of the traverse. During this time of day, as confirmed by wind measurements obtained later, the direction of the wind changed significantly during the traverse. At the end of the traverse, the wind was flowing from the southwest.

NO_2 results are shown in Figure 3; a uniform low level of gas was observed.



LEGEND

DISTANCE: 0 — 2.5 KM

BURDEN: 0 100 200 PPM

FLOW: 0 100 200 MT/D

Figure 2

SO2 TOTAL BURDEN AND MASS FLOW

18 OCTOBER 1971 (1123-1218 PDT)

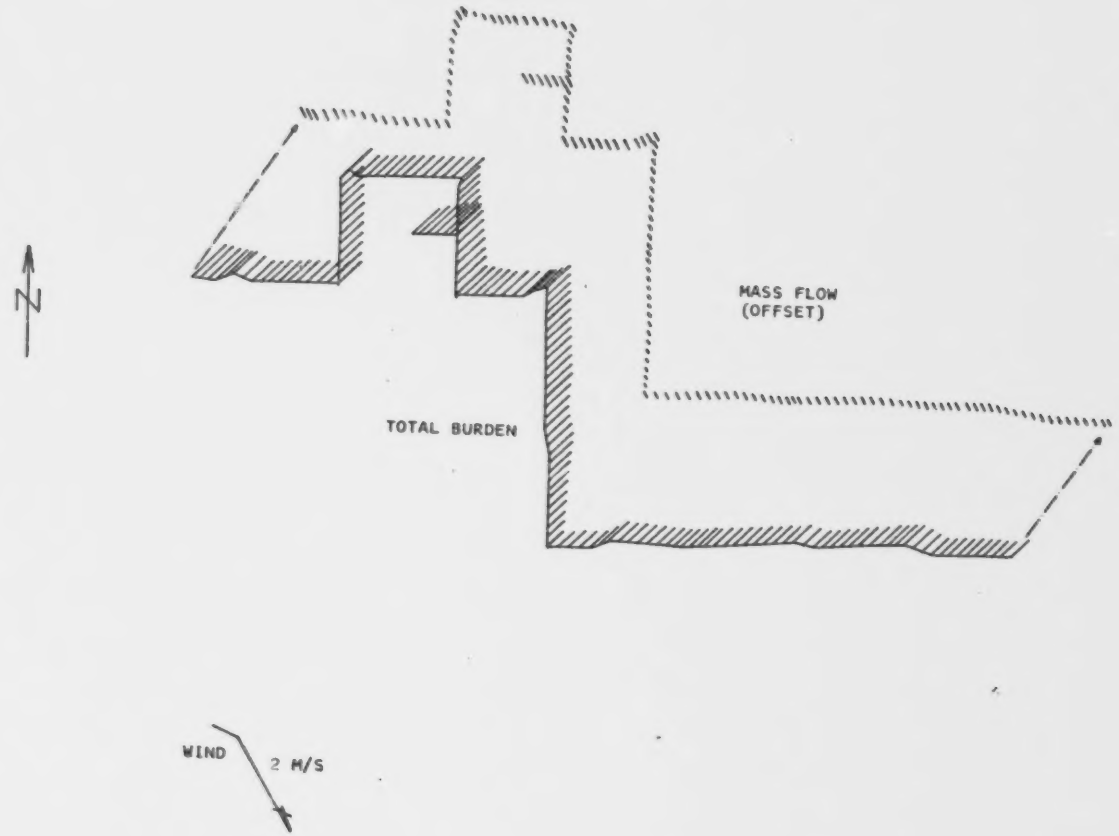


Figure 3

NO_2 TOTAL BURDEN AND MASS FLOW

18 OCTOBER 1971 (1123-1218 PDT)

A second traverse was made along a more northerly route than used previously (Figure 4); a third traverse returned along this same route (Figure 5). The wind was from the southwest. SO_2 flowed from each of the refineries in the area, though no dramatic plumes were observed. An increase in NO_2 was detected along the latter route, which had heavy vehicular flow.

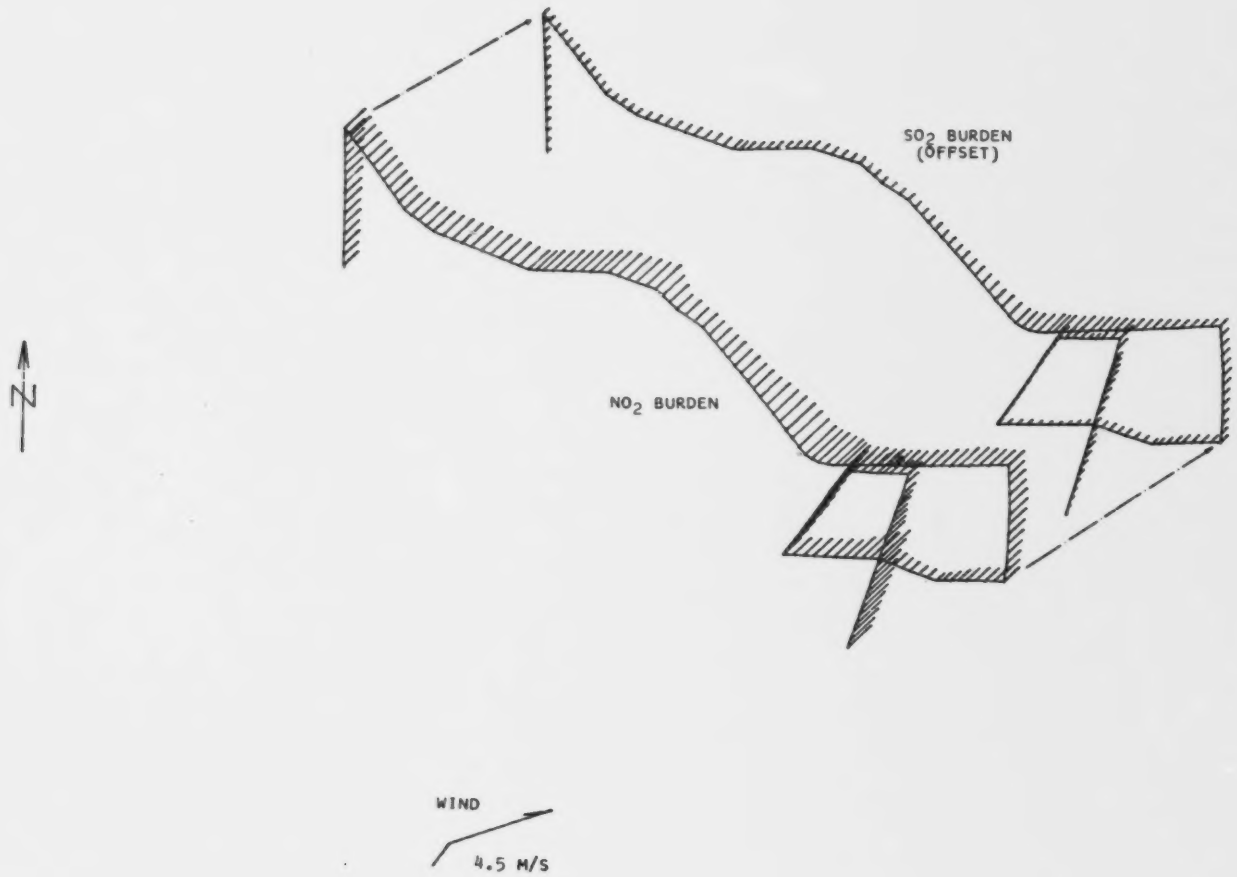
It was concluded that the instrument had been tuned to a less-sensitive correlation position, and that all absorption bands were not used. This results in a loss of sensitivity and an increase in noise.

19 OCTOBER 1971

A repeat of the 18 October traverse was made after realigning the correlation spectrometer. The data were considerably more distinct with the higher sensitivity. The results are shown in Figures 6 and 7.

No SO_2 was measured along the route except in clearly defined plumes downwind of known sources. NO_2 was more prevelant than the previous day. Maps show a distinct buildup of gas downwind of the refinery areas, which is superimposed on the ambient levels. Increased NO_2 was also observed downwind of the refineries at the east end of the traverse.

Emissions on the order of 25 metric tons per day SO_2 and 19 MT/D NO_2 were observed flowing from one refinery.



LEGEND

DISTANCE: 0 2.5 KM

BURDEN NO_2: 0 20 40 PPM

BURDEN SO_2: 0 100 200 PPM

Figure 4

NO_2 AND SO_2 TOTAL BURDEN

18 OCTOBER 1971 (1230-1308 PDT)

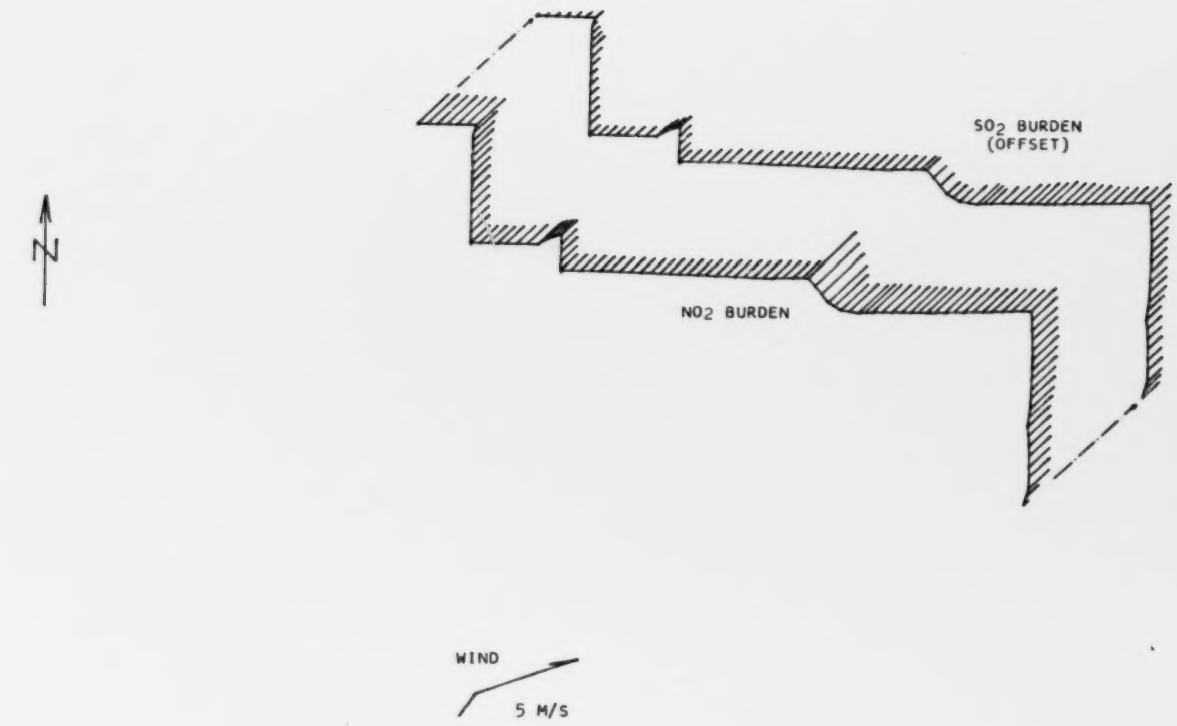


Figure 5

NO_2 AND SO_2 TOTAL BURDEN

18 OCTOBER 1971 (1324-1352 PDT)

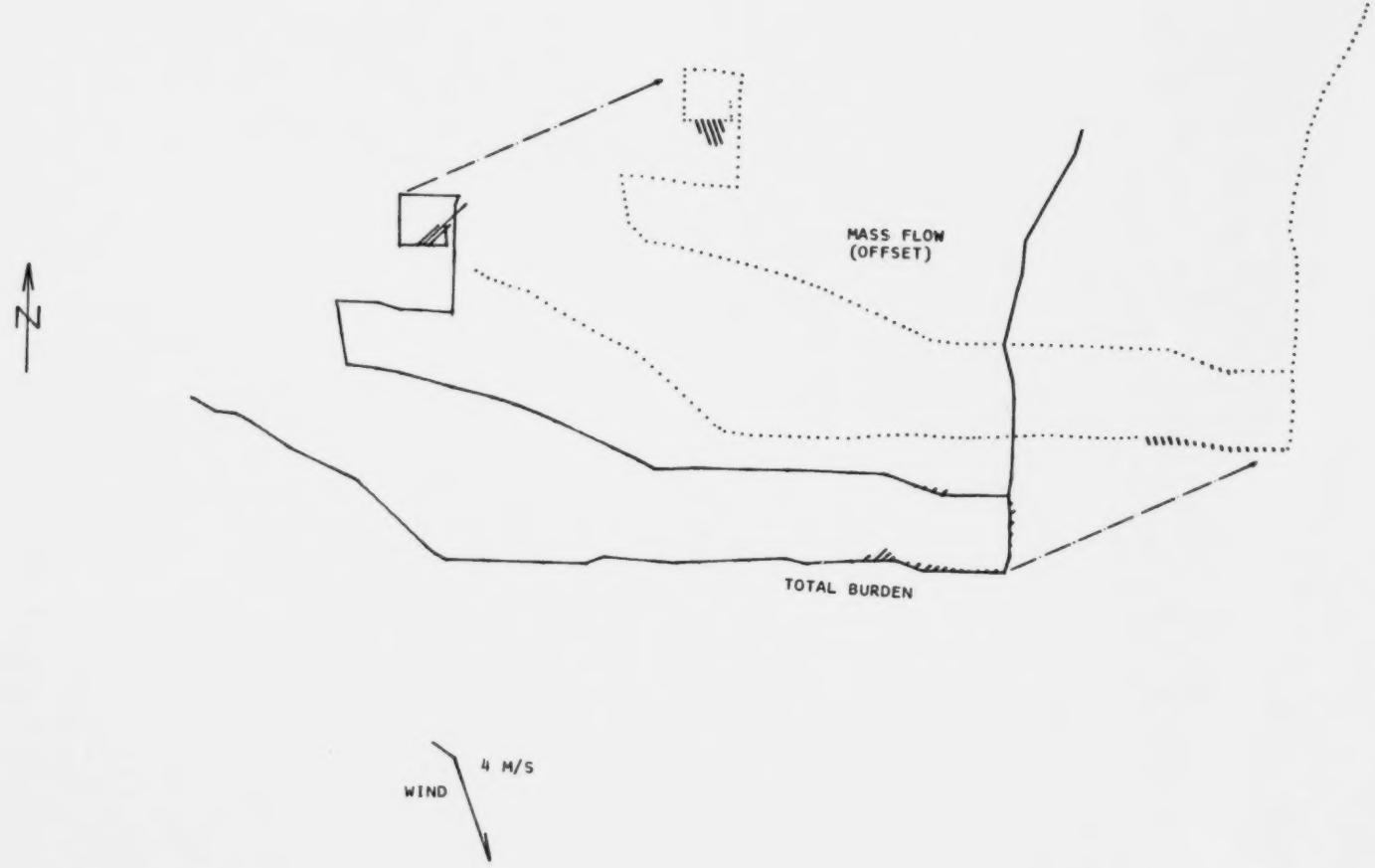


Figure 6

SO_2 TOTAL BURDEN AND MASS FLOW

19 OCTOBER 1971 (1147-1350 PDT)

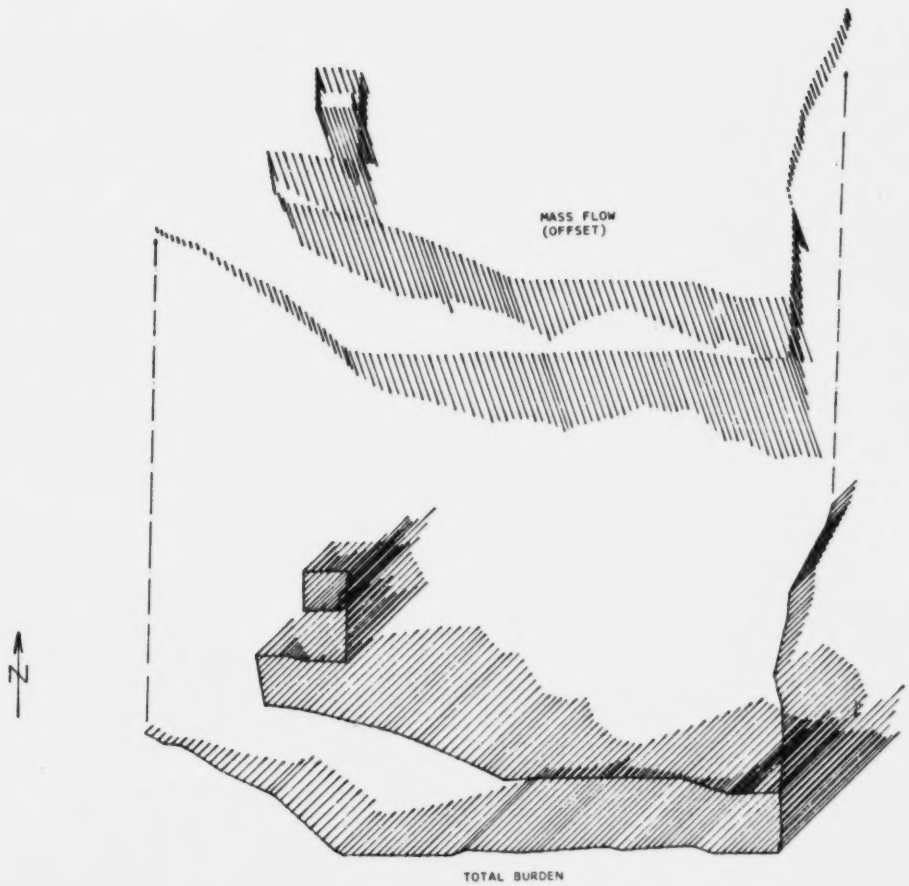


Figure 7

NO_2 TOTAL BURDEN AND MASS FLOW

17 OCTOBER 1971 (1147-1350 PDT)

These compare with the 150 MT/D SO_2 measurement and the 12 MT/D NO_2 flow made on July 16 under Task B.

LONG-LINE MONITORING

A principal objective of the field trials was to experiment with the correlation spectrometer in its "long-line" configuration. The site selected was along the eastern boundary of an oil refinery. The distance between the light source and the receiver was 1235 meters. Figure 8 shows the instrument tent and remote light source at night.

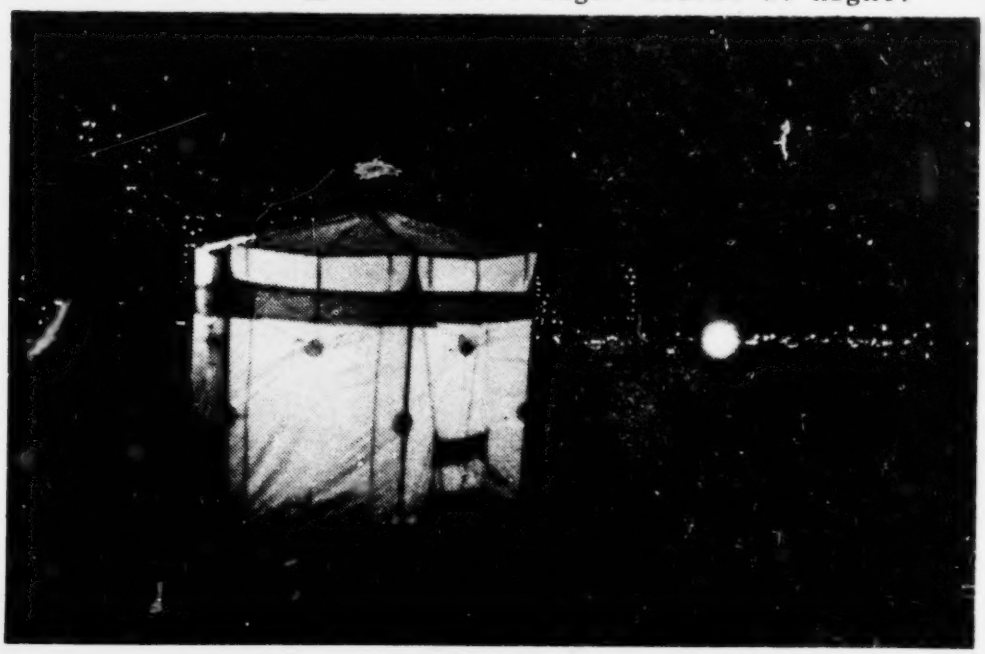


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FIGURE 8

LONG-LINE ALIGHMENT, 1235-METER N-S PATH

The electronically modulated xenon lamp source was mounted on the roof of a service station. The very narrow

beam extended through the lattice work of the refinery to the instrument site, where the beam was on the order of 6 meters wide. This alignment paralleled a major roadway. Even at night it appeared just as another street light except when viewed directly (Figure 8).

Data were gathered between 2040 and 2207 PDT on 19 October and between 1530 and 0530 PDT on 20/21 October. The principal reasons for the interruption of the data were malfunctions of the lamp which did not have an automatic reset circuit. The system was plugged into the overnight lighting network of the service station; when the lights for the station were extinquished for the evening (at 2200 hours), the power surge turned the xenon light off. By the time the COSPEC operator was able to get to the light, the station personnel were gone; attempts to turn it on during the rest of the night were frustrated by problems of getting on the roof. Nevertheless, it was lighted in the evening, but a circuit problem prevented the operation of the modulator. By morning the light had been reactivated. Inadvertently it was turned off by the morning service station crew. In the process, a xenon lamp was burned out. It was later in the day before the lamp was replaced, and the longer period of data were gathered.

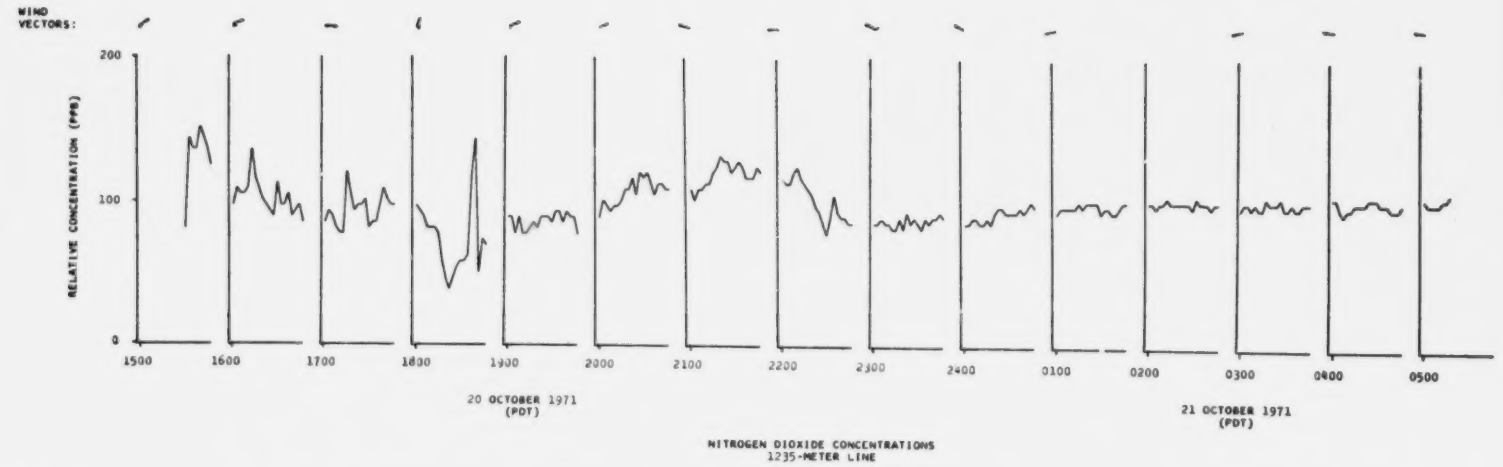
The power surge problem reoccurred on the morning of 21 October ending the data run.

Results of the extended 20/21 October record are shown in Figure 9, together with winds obtained from the local airport, 6 miles northwest. The gas blowing from the refinery passes through the line of sight. When the wind reversed at 2100 hours PDT apparently some of the gas that had blown to the east, was now blown back through the line into the refinery.

Larger concentrations of SO_2 were shown downwind of the refinery. When the winds reversed, this gas appeared to flow back, in lesser concentrations. The NO_2 data, on the other hand, appeared to flow less from the refinery, this may reflect a general increase in ambient level related to the evening traffic hours. In addition, when the wind reversed itself, the NO_2 concentration appeared to increase. This may reflect a conversion from NO during the time the gas was east of the line of sight.

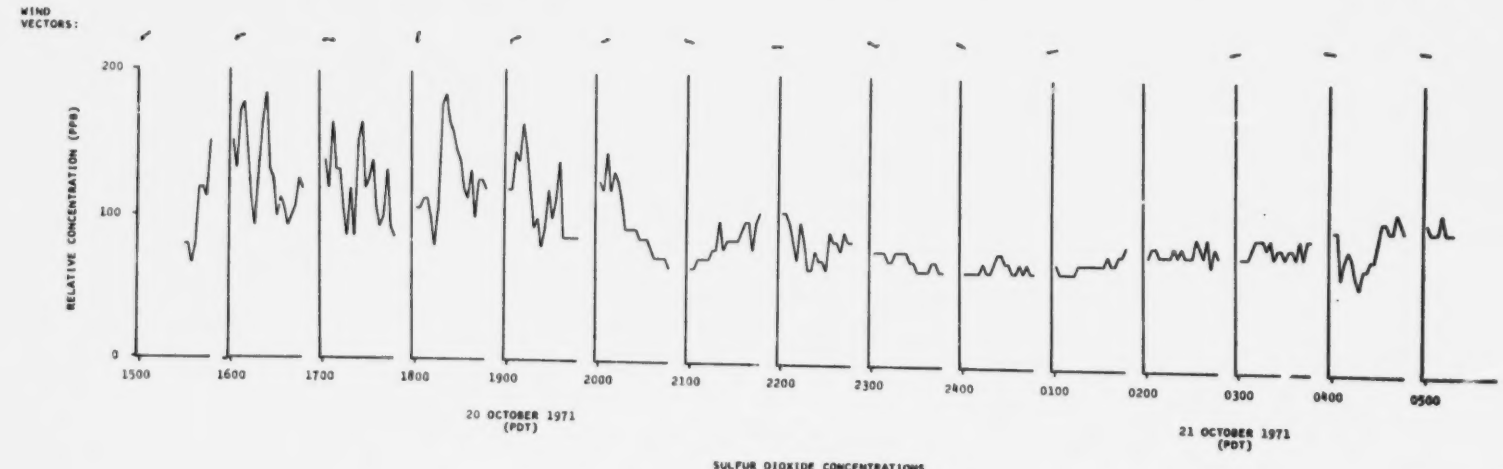
Variations of 100 ppb were measured in both target gases; noise levels were on the order of 5 ppb.

The problem of obtaining a zero base was not resolved in these tests. Attempts were made to measure gas over a very short path, thereby showing a zero or low gas condition. Trouble in obtaining a supply of sufficient electrical energy (to strike the xenon lamp) at the instrument site precluded obtaining a valid zero reference. Therefore, the data are relative. It would appear, nevertheless, that data obtained



NITROGEN DIOXIDE CONCENTRATIONS
1235-METER LINE

FIGURE 9



SULFUR DIOXIDE CONCENTRATIONS
1235-METER LINE

during the early morning low level of activity would be a reasonable low-gas condition. But, it should be pointed out that the absolute nature of these graphs is not determined.

The absolute value of energy absorption is inherent in the data, within the instrument, but has not been displayed during these tests. Prototype correlation spectrometers displayed an evelope of oscillations on an analog record; the width of the envelope was a function of absolute absorption. In this later version of the instrument, this width has been further processed to be shown as an amplitude variation on the chart record.

It is also worth noting that these data reflect the spatially integrated concentration of gas over 1235 meters. A peak variation of 100 parts per billion is equivalent to 124 parts per million-meters. This effect could be caused by a 10-meter wide cloud of gas with an average concentration of 12.4 parts per million -- or any number of variations.

The long-line data gathered on 19 October between 2040 and 2207 PDT showed variations of 30 ppb SO_2 and 15 ppb NO_2 under easterly wind conditions. Noise levels were similar to the 20/21 October data.

EMISSION EVALUATION

On 22 October 1971 two correlation spectrometers were used at the Kaiser Steel Company, Fontana, California, to measure the SO_2 of a single stack venting effluent from dual

sources in their sinter plant. Concurrently samples were drawn from each flu for one hour and these were analyzed by wet-chemical procedures for SO_2. The wind was blustery, and conditions were poor for the precise plume measurement required for accurate mass flow calculations; yet the opportunity was seized. Mean calculated flow rates of 24.3 and 24.9 metric tons per day, respectively, were obtained for the two sets of remote-sensing data gathered over a thirty-minute period. The wet-chemical results reported a combined flow of 17.3 metric tons per day for one hour.

The correlation spectrometers were used in the vertical-viewing, passive mode to traverse adjacent to and around the sinter plant stack. Eight kilometer-long completely circumnavigating traverses were used to measure the emission data.

Since SO_2 was the target gas, the SO_2 channel of each instrument was connected to one trace of a two channel recorder. Figure 10 is a sample of an actual plume trace gathered. Overhead obstructions are obvious offsets on the data.

The emissions were calculated by computer using burden values every 50 meters or closer as transcribed from the strip chart record. A finite period of time was necessary to circumnavigate the stack; the average travel time was 5.5 minutes. On this date the wind data were highly variable, as stated, and Figure 11 shows the wind speed as obtained from an anemometer located at 40 meters above the ground approximately 100 meters

from the sinter stack. Times of measurement are also noted; emission calculations are linearly related to wind speed.

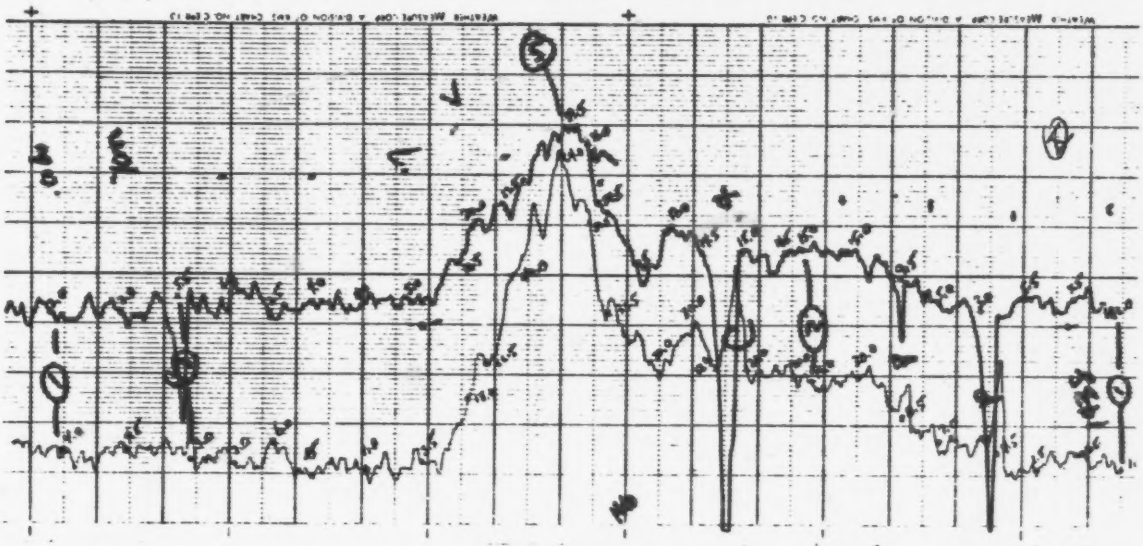


FIGURE 10
ACTUAL DATA OBTAINED DURING
SINTER PLANT EMISSION MEASUREMENTS (ONE KILOMETER TRAVERSE)

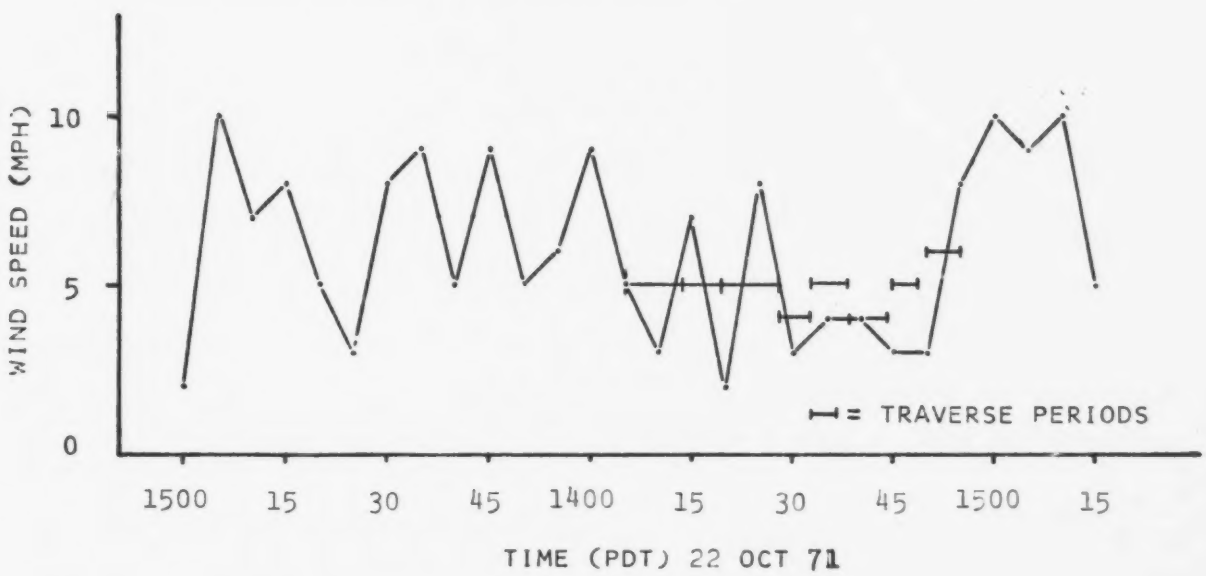


FIGURE 11
WIND SPEED AT 40 METERS ABOVE SURFACE
AND WINDS SELECTED FOR CALCULATIONS

By enclosing the source all of the flow into the prescribed area is deducted from the total outflow. Only gas produced inside the area is determined. The following table lists these values:

Table 1

SO_2 EMISSION DATA FOR CIRCUMNAVIGATION TRAVERSES

Time 22 Oct 71 (PST)	Wind SPEED (MPH)	EPA COSPEC (MT/D)	EMI COSPEC (MT/D)
1406-1413	5	25.7	25.8
1413-1419	5	29.9	29.1
1419-1427	5	21.5	22.4
1427-1432	5	26.0	23.4
1432-1438	4	14.3	15.7
1438-1443	5	18.9	21.6
1443-1448	4	27.4	25.1
1450-1456	6	30.9	36.2
Averages:		24.32	24.91

Knowledge of wind speed becomes the dominant factor and is the reason why a number of measurements should be made at each site. For these traverses the wind speeds to the nearest mile per hour were selected at the peak of the plume; this was approximately 5 mph. During the traverse time the wind was measured to vary between 2 and 8 mph; thus, "noise" contributed by wind was a great as plus-or-minus 60%.

The Kaiser Steel Company cooperated fully in this evaluation. The flues feeding the stack were monitored for an hour during the course of our experiment and solutions were analyzed using wet-chemical procedures. They measured gaseous SO_2 of 647 parts per million in the West Baghouse and 496 ppm in the East Baghouse. A sampled average value of 577 ppm was reported, and a flow rate of 272,000 standard cubic feet per minute was estimated from current readings compared to previous velocity relationships. These combined values are equivalent to 17.3 metric tons per day, 70% of the value measured by the correlation spectrometer.

CONCLUSION

The results obtained with two correlation spectrometers were shown to compare within 2% in a test of their use to measure SO_2 emissions. Simultaneous wet-chemical, in-stack SO_2 concentration measurements resulted in hour-long comparable data which were 70% of the remote sensor values. The correlation spectrometer measurements, linearly dependent on wind speed, were undertaken during variable wind conditions which contributed as much as ± 30% shift in wind speeds. Thus, the relatively close agreement of the independent methods is excellent.

Long-line, spatial-integrated monitoring was conducted along one boundary of an oil refinery in Southern California. This was the initial test of the latest modification to the Barringer spectrometer, one which allows a narrow-filtered observation of an electronically modulated artificial light source. Day and night variations in SO_2 and NO_2 were measured along a 1235-meter path. The system sensitivity was on the order of 5 parts per billion for both gases. When the wind blew across the refinery, variations in excess of 100 ppb were frequent; when the line was upwind, variations were as small as 10 ppb. A zero reference was not obtained to confirm the baseline for these data.

Regional total burden surveys were made by driving around an industrial area, and the results were used to compute mass flow maps in the area. While plumes were distinct from each major source, these data were generally uniform over the ten-mile distance. Except, NO_2 data measured on 19 October showed clearly defined plumes for distances in excess of five miles. As reported in Task B, near a power plant and steel complex, NO_2 increased in amount downwind of the source.

The correlation spectrometer was used extensively for one week in three separate applications -- regional surveying, concentration monitoring, and for emission measurements.